

Enhanced thermoelectric properties of poly(3,4-ethylenedioxythiophene) thin films treated with H₂SO₄

Jiao Wang ^a, Kefeng Cai ^{a,*}, Shirley Shen ^b

^aKey Laboratory of Advanced Civil Engineering Materials of Ministry of Education, Functional Materials Research Laboratory, School of Materials Science & Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, China

^bCMSE, CSIRO, 37 Graham Road, Highett, VIC 3190, Australia



ARTICLE INFO

Article history:

Received 12 July 2014

Received in revised form 4 September 2014

Accepted 6 September 2014

Available online 18 September 2014

Keywords:

Thermoelectric properties

Vapor-phase polymerization

Poly(3,4-ethylenedioxythiophene)

Film

ABSTRACT

Poly(3,4-ethylenedioxythiophene)-tosylate-polyethylene glycol-polypropylene glycol-polyethylene glycol (PEDOT-Tos-PPP) films were prepared via a vapor phase polymerization (VPP) method. The thermoelectric (TE) properties of the films before and after treated with H₂SO₄ at different concentrations were measured at 295 K. The TE properties of the films have been significantly improved by the H₂SO₄ treatment. For example, after treated with H₂SO₄ at 1 M, the electrical conductivity of the film has increased remarkably from 944 to 1750 S cm⁻¹, the Seebeck coefficient of the film reduced slightly from 16.5 to 14.6 μ V K⁻¹, and the thermal conductivity decreased from 0.495 to 0.474 W/mK. Hence, the ZT value at 295 K has increased from 0.016 to 0.024. The electrical conductivity (Seebeck coefficient) of the untreated and 1 M H₂SO₄ treated PEDOT-Tos-PPP films decreases (increases) with increasing temperature from 295 to 375 K. And the power factor of the films monotonically increases with temperature. The power factor at 375 K of the 1 M H₂SO₄ treated film is almost twice as high as that at 295 K. Atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS) analyses, and the thickness measurement of the films indicate that the tri-block copolymer PPP have been removed from the PEDOT-Tos-PPP films after the H₂SO₄ treatment, and the UV-Vis-NIR absorption spectroscopy and Raman spectroscopy analyses reveal an increasing in the doping level in the PEDOT chains after the H₂SO₄ treatment. Therefore, the TE properties enhancement may be attributed to the combined effects of the removal of the insulating PPP from the PEDOT-Tos-PPP film, increase the doping level and conformational change of the PEDOT chains resulted from the H₂SO₄ treatment.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Thermoelectric (TE) materials have recently attracted worldwide attentions because of their great potential applications in fields such as solid-state refrigeration and

power generation without any moving parts. The TE performance of a material can be evaluated by its dimensionless figure of merit $ZT = \alpha^2 \sigma T / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity, respectively. TE material with high ZT requires a high α , a high σ but a low κ ; however, it is very difficult to modulate the three parameters synchronously to get a high ZT value because they are dependent on each other.

* Corresponding author.

E-mail address: kfcai@tongji.edu.cn (K. Cai).

Until now, most of the previous efforts in TE community have been mainly focused on traditional inorganic TE materials, including Bi–Te based alloys [1] and PbTe based alloys [2,3]. These inorganic TE materials show high ZT values, but they consist of heavy or rare metals, which are hazardous, expensive and difficult to recycle, and they usually need a complicated preparation processing. Although conducting polymers usually have power factors (PF , $S^2\sigma$) ranging from 10^{-6} to $10^{-10} \text{ W m}^{-1} \text{ K}^{-2}$, which are about 3 orders of magnitude lower than those of the state-of-the-art inorganic TE materials [4–7], they possess unique features such as low thermal conductivity, low density, low cost, easy synthesis, and relatively facile to be processed into versatile forms, and they are very promising for mass-production and large-area applications. Hence, more and more attentions have recently been paid to the TE properties of conducting polymers and polymer based nanocomposites [7–16] and much progress has been made [17–19]. For example, a tosylate (Tos) optimum doped poly(3,4-ethylenedioxythiophene) (PEDOT, see Fig. 1a) film with $ZT = 0.25$ at room temperature (RT) [20] and a poly(styrenesulfonate) (PSS) optimum doped PEDOT film with $ZT = 0.42$ at RT [21] were successively reported. The TE properties of PEDOT:PSS can be optimized through chemically or electrochemically control of their oxidation level [22–24], as well as treatment with high-boiling-point solvents [21,25]. PEDOT-Tos [26] can be considered as the polyanion PSS in PEDOT:PSS being replaced by a small anion Tos, preventing the excess of insulating phase generated with polyanions, and as a result the electrical conductivity of PEDOT-Tos films is higher than that of PEDOT:PSS films.

Usually, conducting polymers are synthesized by either a chemical oxidative polymerization or an electrochemical polymerization of its monomer in a liquid phase [27,28]. Recently, a new and more effective method has been developed for formation of conducting polymers, which is called vapor-phase polymerization (VPP) method. Pioneering work on VPP done by Winther-Jensen and West, achieved an electrical conductivity of $\sim 1000 \text{ S cm}^{-1}$ of a PEDOT-Tos film, using an oxidant iron p-toluenesulfonate ($\text{Fe}(\text{Tos})_3$, see Fig. 1b) coupled with a volatile base pyridine

[29]. Fabretto et al. [30] prepared a PEDOT-Tos film with a conductivity of ca. 3400 S cm^{-1} , using a tri-block copolymer polyethylene glycol–polypropylene glycol–polyethylene glycol (PPP, see Fig. 1c) as an inhibitor via a vacuum VPP method. Compared with other methods, VPP is simpler, and more rapid and convenient to manufacture highly conductive polymer films. To the best of our knowledge, almost all the studies on high conducting PEDOT film via the VPP method are for transparent conducting electrodes. The TE properties of high conducting PEDOT film prepared via VPP method have rarely been reported.

In this paper, successful fabrication of PEDOT-Tos films via a VPP method is reported. The TE properties of the films before and after the H_2SO_4 treatment have been investigated. The TE properties were significantly improved by the treatment. To understand the enhancement mechanism, the films have also been characterized by X-ray photoelectron spectroscopy (XPS), UV–Vis–NIR absorption spectra and Raman spectroscopy, respectively.

2. Experimental

Iron p-toluenesulfonate heptanedionate ($\text{Fe}(\text{Tos})_3 \cdot 6\text{H}_2\text{O}$) and tri-block copolymer polyethylene glycol–polypropylene glycol–polyethylene glycol (PPP) $M_w = 5800 \text{ Da}$. were obtained from Aldrich. 3,4-Ethylenedioxythiophene (EDOT) monomer was purchased from Bohong Electronic Chemicals Co., Ltd, Yancheng, China. All chemicals were used as received without further purification.

PEDOT-Tos-PPP films were prepared by a VPP technique described by Fabretto et al. [30]; however, our VPP process was carried out at atmosphere rather than under vacuum. PEDOT films were synthesized on $2.5 \times 3.5 \text{ cm}^2$ glass substrates, which were cleaned by using detergent, ethanol and deionized water sequentially in an ultrasonic bath for 30 min.

Synthesis was carried out using an oxidant solution containing 20% $\text{Fe}(\text{Tos})_3 \cdot 6\text{H}_2\text{O}$ and 20% PPP in an ethanol and butanol (1:1) solution. The tri-block copolymer PPP was added as an inhibitor to the oxidant solution to control the kinetics of the polymerization as well as a template for growing the PEDOT-Tos-PPP films by the VPP technique

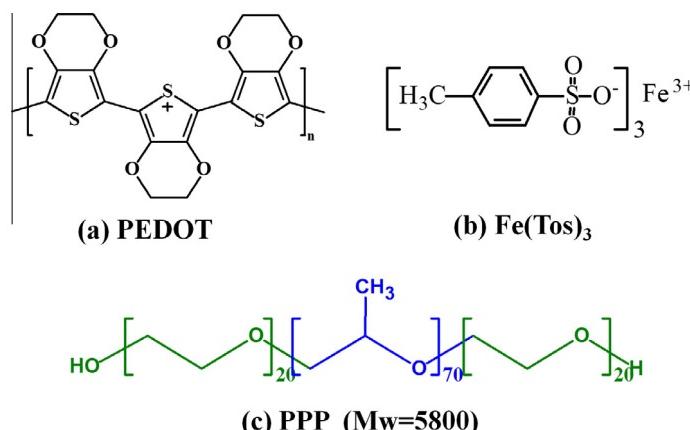


Fig. 1. Molecular structures of (a) PEDOT (b) $\text{Fe}(\text{Tos})_3$ and (c) tri-block copolymer PPP.

[31]. The oxidant solution was first spin-coated onto the cleaned glass substrates, and then the samples were transferred into a polymerization chamber and exposed to a vapor of EDOT at 50 °C for 30 min. After the polymerization process, the excess Fe(Tos)₃ and unreacted monomers were removed by washing with ethanol.

In order to further enhance the TE properties, the films were post treated by H₂SO₄. The H₂SO₄ treatment was performed by dropping a 200 μL H₂SO₄ solution on a pristine film on a hot plate at 140 °C for about 10 min. The films were dried and cooled down to RT, and then were rinsed with ethanol for three times. The concentration of the H₂SO₄ solution used was 0.5, 0.75, 1.0, 1.25 and 1.5 M, respectively. Finally, the H₂SO₄-treated films were dried at 60 °C under vacuum for 24 h again.

2.1. Characterization

Seebeck coefficient was obtained from the slope of the linear relationship between thermal electromotive force and temperature difference (~10 K) of two points of each film. Electrical conductivity was measured using a steady-state four-probe technique with a square wave current (~10 mA in amplitude). Thermal conductivity was measured by TC3010 using the transient hot wire method (Xia Xi Electronic Technology Co., Ltd, Xi'an, China). Samples for thermal conductivity measurements were prepared by multi-layer structures (each layer formed by repeating the above-mentioned polymerization process) to achieve a sample thickness large enough for accurate measurement. The thicknesses of the polymer films were determined with a Dektak 150 profilometer.

Atomic force microscope (AFM, SPA-300HV) was used to examine the morphology of the polymer films. XPS was used to investigate incorporation of different counterions into PEDOT films with Al K α radiation (1486.6 eV) using an ESCALAB 250Xi system X-ray photoelectron spectrometer equipment. The UV-Vis-NIR absorption spectra of the polymer films were taken with a JASCO V570 UV-Vis-NIR spectrometer. The Raman spectra of the PEDOT-Tos-PPP films were examined by a Jobin Yvon HR800 Raman spectrometer using a laser diode at an excitation wavelength of 514.5 nm.

3. Results and discussion

Fig. 2a shows the room-temperature (295 K) electrical conductivity, Seebeck coefficient, and power factor for the PEDOT-Tos-PPP films before (corresponding to the concentration of H₂SO₄ being 0) and after treated with different concentrations of H₂SO₄. The electrical conductivity quickly increases after treated with low concentrations of H₂SO₄ (from 944 S cm⁻¹ untreated to 1750 S cm⁻¹ treated with 1 M H₂SO₄), and then increases very slowly with further increase in the concentration of H₂SO₄ (≥ 1 M). It is reported that electrical conductivity enhancement of PEDOT:PSS films is strongly dependent on dielectric constant of the chemicals used for treatment [32–34]. Solvent with higher dielectric constant induces a stronger screening effect between counterions and charge carriers, which in

turn reduces the Coulomb interaction between PEDOT and PSS dopant [35]. The PEDOT-Tos-PPP films may be similar to the PEDOT:PSS films. H₂SO₄ with high dielectric-constant (~101) can trigger phase separation between the conducting PEDOT chains and insulating PPP chains and then the PPP chains are washed away, leading to more PEDOT domains in the film, hence generates a higher electrical conductivity.

The Seebeck coefficient of the films increases very slowly with the increasing of concentration of H₂SO₄ (from 16.5 μ V K⁻¹ to 14.5 μ V K⁻¹). The Seebeck coefficient values are lower than that reported in Ref. [31], which should be due to different synthesis conditions. Although it is common for conducting polymers to show an inverse relationship between the Seebeck coefficient and the electrical conductivity [22,24,36], the increase in the electrical conductivity is much quicker than the decrease in the Seebeck coefficient, resulting in a significant improvement in the power factor after the H₂SO₄ treatment (from 25.7 μ W m⁻¹ K⁻² for the pristine PEDOT-Tos-PPP film to a maximum power factor of 37.3 μ W m⁻¹ K⁻² treated with 1.0 M H₂SO₄). The film formed wrinkles and was easily peeled off from the substrate when the concentration of H₂SO₄ was more than 1.5 M. Therefore, 1.0 M H₂SO₄ aqueous solution was chosen for the post-treatment.

In order to understand the conduction mechanism of the untreated and H₂SO₄ treated films. The electrical transport properties of the prepared PEDOT-Tos-PPP and the 1 M H₂SO₄ treated films were further measured from 295 to 375 K. The electrical conductivity of both films decreased with increasing temperature (Fig. 2b), showing a metallic or heavily doped semiconducting behavior. This result is in agreement with that reported in Ref. [31]. The inset in Fig. 2b shows the plots of ln(σ) vs. T^{-1/3}. It is found that the plots exhibit straight lines for the two film samples in the range of 295 K < T < 375 K, suggesting that the temperature dependences of the electrical conductivity are consistent with the characteristics of variable range hopping conduction [37].

Fig. 2c shows the temperature dependence of Seebeck coefficient of the untreated and H₂SO₄ treated films. At a given temperature in all the temperature range measured, the Seebeck coefficient of treated film is lower than that of the untreated one. The Seebeck coefficients of the two samples both increase with temperature increasing from 295 to 375 K, and that of the H₂SO₄ treated film increases quicker than that of the untreated one, so that at 375 K it gets close to that of the untreated film. The power factor ($\sigma\alpha^2$) of the treated film is always higher than that of untreated one because of the former having much higher electrical conductivity in the temperature range measured, and the power factor rises with temperature and reaches 58 μ W m⁻¹ K⁻² at 375 K for the treated film (Fig. 1d).

The thermal conductivity of the pristine and 1.0 M H₂SO₄-treated PEDOT-Tos-PPP films is 0.495 ± 0.005 and 0.474 ± 0.005 W/mK, respectively. After the treatment the thermal conductivity slightly reduced, which is consistent with the results obtained in DMSO-mixed and EG-mixed PEDOT:PSS films [21]. The values are slightly higher than that of the previous reported commercial PEDOT:PSS film [21], but still much lower than that of conventional

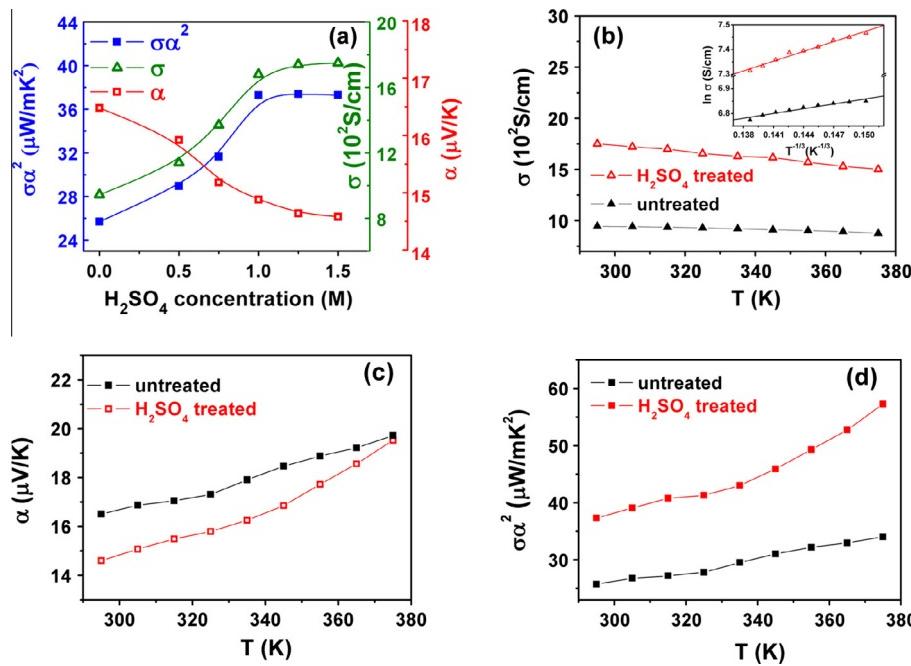


Fig. 2. (a) TE properties of the PEDOT-Tos-PPP films at room-temperature (295 K) before and after treated with different concentration of H_2SO_4 solutions and the temperature dependence of (b) electrical conductivity (c) Seebeck coefficient (d) power factor of the untreated and 1 M H_2SO_4 treated films from 295 to 375 K. The inset in (b) shows the relation of $\ln(\sigma)$ vs. $T^{-1/3}$.

inorganic TE materials. The intrinsically low κ of PEDOT film provides it a great potential for TE applications. Based on the measured values, the maximum ZT value of the 1.0 M H_2SO_4 treated PEDOT-Tos-PPP film is ~ 0.024 at 295 K, indicating that H_2SO_4 treatment is efficient to improve the TE property of PEDOT-Tos-PPP films. The ZT value of the 1.0 M H_2SO_4 treated film at 375 K was estimated to be ~ 0.046 using its power factor at 375 K and thermal conductivity (0.474 W/mK) at 295 K since the thermal conductivity of PEDOT is insensitive to temperature [38].

The thickness of the pristine and 1.0 M H_2SO_4 -treated PEDOT-Tos-PPP films is 140 ± 5 and 110 ± 5 nm, respectively. The film thickness was reduced by about 20% after the H_2SO_4 treatment. The 30 nm thickness loss after treatment with 1.0 M H_2SO_4 gives a clue that PPP or Tos or both PPP and Tos are removed from the film surface as the hydrophobic PEDOT is insoluble in highly hydrophilic H_2SO_4 (Similar phenomenon was observed in the PEDOT:PSS film treated with EG in Ref. [21] and treated with methanol in Ref. [39], where the authors claimed that PSS was removed by the treatment). Hence, the PEDOT-Tos-PPP films before and after the 1 M H_2SO_4 treatment were further examined by various characterization methods.

Fig. 3 shows UV-Vis-NIR absorption spectra of untreated and H_2SO_4 -treated PEDOT-Tos-PPP films. The strong absorption band in the UV range (200–300 nm) originates from the aromatic ring of Tos [40]. The intensity of the strong absorption band remarkably drops after the H_2SO_4 treatment, which indicates partially removal of Tos[−] from the PEDOT-Tos-PPP film. Several previous works

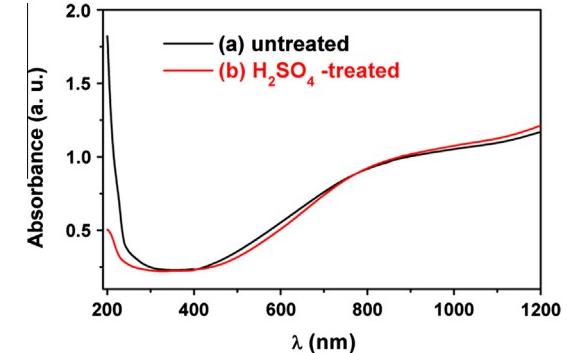


Fig. 3. UV-Vis-NIR absorption spectra of untreated and H_2SO_4 -treated PEDOT-Tos-PPP films. Inset shows digital photographic images of untreated and H_2SO_4 -treated PEDOT-Tos-PPP films.

showed that the π -to- π^* transition is in the range of 580–600 nm, and that their relative intensity decreases as the doping level increases [20,41,42]. The band increase around near infrared region (NIR) (above 1000 nm) is associated with an increase of the doping level and the formation of bipolarons [43]. Fig. 3 shows that the relative intensity of the π -to- π^* transition peak (around 600 nm) decreases after the H_2SO_4 treatment, and that the absorbance band around NIR increases. The results indicate that the doping level of PEDOT increased after the H_2SO_4 treatment and that the concentration of bipolarons increased. Thus, the electrical conductivity increases after the H_2SO_4 treatment.

XPS survey spectra of the PEDOT-Tos-PPP films without and with H_2SO_4 treatment are shown in Fig. 4a. Four peaks

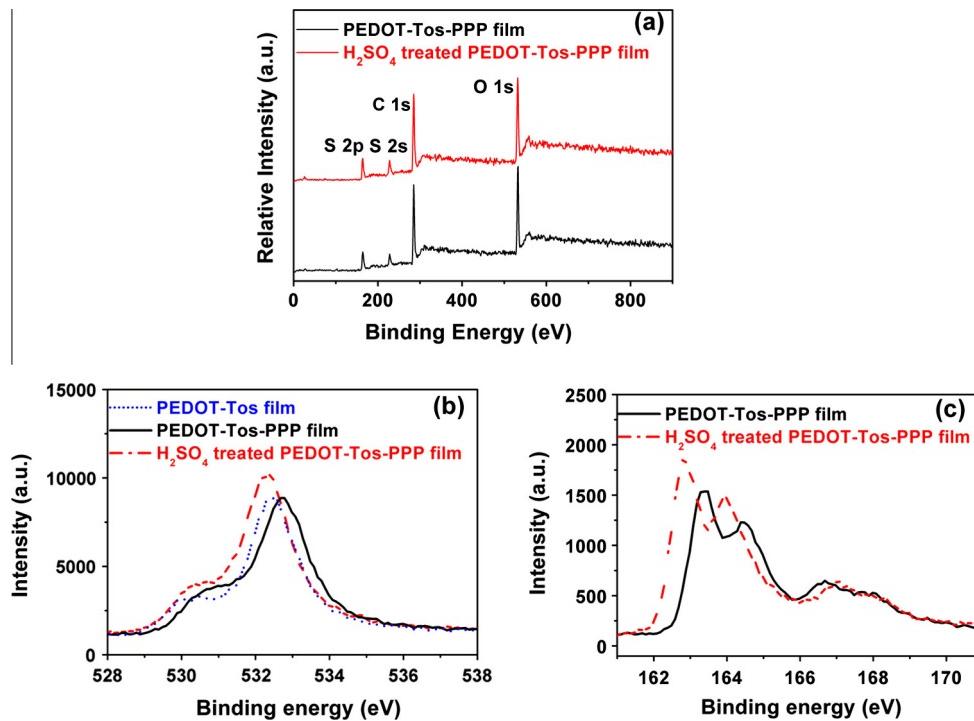


Fig. 4. XPS analysis of untreated and H_2SO_4 -treated films (a) survey spectrum (b) O_{1s} spectra (c) S_{2p} spectra.

at 164, 228, 285, and 532 eV correspond to the S_{2p} , S_{2s} , C_{1s} , O_{1s} peaks, respectively. In the survey spectra the peak intensity ratio of S/C peaks increased from 0.34 to 0.42 after the H_2SO_4 treatment, and that of O/C peaks decreased from 1.3 to 1.1. What is the real reason for the change in the S/C and O/C peak intensity ratios?

The tri-block copolymer PPP is a hydrocarbon based polymer with oxygen incorporated in the backbone structure, and several previous O_{1s} studies have revealed that a significant amount of PPP remains embedded within the PEDOT polymer matrix of PEDOT-Tos films [44,45]. Hence, O_{1s} and S_{2p} spectra have been further studied here. Fig. 4b shows the O_{1s} spectra for a PEDOT-Tos film (PEDOT film without tri-block copolymer PPP, prepared by the same method as for the PEDOT-Tos-PPP films), an untreated PEDOT-Tos-PPP film, and a 1.0 M H_2SO_4 treated PEDOT-Tos-PPP film. The strongest peak of O_{1s} of the PEDOT-Tos film is located at 532.2 eV, and that of the PEDOT-Tos-PPP film is at 532.7 eV, which shifts to a slightly higher energy level compared to that of the PEDOT-Tos film. Interestingly, the strongest peak of the H_2SO_4 treated PEDOT-Tos-PPP film shifts back to the lower energy level at 532.2 eV. This indicates that the tri-block copolymer PPP incorporated into the PEDOT during the processing, which is consistent with that reported in Ref. [45] and that all or almost all of the PPP was removed from the film after the H_2SO_4 treatment, which leads to a significant reduction in film thickness and the enhancement of the electrical conductivity of the film as PPP is insulating.

The two XPS bands between 166 and 170 eV are the S_{2p} bands of the sulfur atoms in Tos^- ion from $\text{Fe}(\text{Tos})_3$,

whereas the two XPS bands between 162 and 166 eV are the S_{2p} bands of the sulfur atoms in PEDOT [26,46]. After the H_2SO_4 treatment, the S_{2p} bands intensity of the sulfur atoms in Tos^- ion relatively decreases compared with that of the sulfur atoms in PEDOT. This indicates partially removal of Tos^- from the PEDOT-Tos-PPP film, which agrees with the result obtained from UV-Vis-NIR spectra (see Fig. 3). On the other hand, it can be seen from Fig. 4c that the S_{2p} bands of the sulfur atoms in PEDOT shifted slightly to a lower energy level while the S_{2p} bands of the sulfur atoms in Tos^- shifted slightly to a higher energy level after the H_2SO_4 treatment. The former shift was also reported in Ref. [32], which may be because of PPP and PEDOT being two different polymers; the binding between them is very difficult, leading to a high binding energy of PEDOT-Tos-PPP film. When the insulating PPP was removed from the PEDOT-Tos-PPP film after the H_2SO_4 treatment, the binding energy of the film would decrease. The latter shift may be due to a replacement of some Tos^- anions by HSO_4^- ions [40] or SO_4^{2-} ions [47], or both of them during an ion exchange process. Combined with the results of S_{2p} spectra and UV-Vis-NIR spectra (the doping level is increased), it is deduced that lots of Tos^- ions were replaced by SO_4^{2-} ions as the counter anions of PEDOT. This is because the Tos^- and HSO_4^- only carry one negative charge, it is more probable for them to create polaronic states, whereas the SO_4^{2-} ions are double charged, increasing the possibility of creating bipolarons in the PEDOT backbone. In this way, the partial replacement of the Tos^- by SO_4^{2-} ions increases the bipolaron population during an ion exchange process, and, as a

consequence, the doping level is increased. In addition, the replacement of some Tos^- ions by SO_4^{2-} ions in the film, there will be a Coulomb force between SO_4^{2-} and the S^+ associated with the PEDOT backbone, which will affect the conformation of the PEDOT chains from a coiled to a linear configuration [47].

Raman spectroscopy is one of the most useful tools for studying the doping behavior of conjugated polymers. We also used it to confirm the presence of doping phenomena after the H_2SO_4 treatment of the PEDOT-Tos-PPP film. Fig. 5 shows the Raman spectra of the PEDOT-Tos-PPP film before and after the H_2SO_4 treatment. The band at 990 cm^{-1} corresponds to the deformations of oxyethylene ring, that at 1265 cm^{-1} corresponds to the symmetric $\text{C}_\alpha-\text{C}_\alpha'$ (inter-ring) stretching, that at 1365 cm^{-1} corresponds to the symmetric $\text{C}_\beta-\text{C}_\beta$ stretching, and that at 1507 cm^{-1} corresponds to the asymmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching [48]. The strongest symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching peak at 1434 cm^{-1} become broader and exhibited blue-shift after the H_2SO_4 treatment, and similar phenomenon was also reported in Refs. [49–51]. In Ref. [49] the authors claimed that the symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching vibration, is a combination of two separate bands, one of which is due to the symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching vibration from the PEDOT segments involving the neutral structure (centered at 1413.5 cm^{-1}) and the other is due to symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching vibration from the PEDOT segments involving the oxidized structure (centered at 1444.5 cm^{-1}). The integrated intensities of these two symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching bands vary with the doping level, i.e. the degree of oxidation in the PEDOT polymeric structure. This explains the shift in wavenumber and the change in the shape of the combined symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching band when the doping level in the polymer is changed. As the doping level becomes lower, the combined band would be more dominated by the symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching vibration due to the neutral structure, and is therefore observed to move towards lower wavenumbers (red-shift), while the result is opposite when the doping level becomes higher [49]. In this work, the symmetric $\text{C}_\alpha=\text{C}_\beta(-\text{O})$ stretching band shifted to higher wavenumber (blue-shift, see the inset of Fig. 5), indicating that the

doping level increases, which agrees with the result observed in UV-Vis-NIR spectra (Fig. 3).

To obtain further information for the mechanism of electrical conductivity enhancement and to investigate the possible changes in the morphology and correlation between morphology and electrical conductivity, AFM images were taken and are shown in Fig. 6. The topographic image (Fig. 6a₁) and phase image (Fig. 6a₂) show that the pristine film mainly consists of two kinds of grains: one is small ($\sim 35\text{ nm}$) and spherical and the other is bigger ($\sim 100\text{ nm}$). By comparing with the AFM image of PEDOT:Tos film (see Supporting materials), it is known that the small and spherical grains are PEDOT:Tos and the bigger grains shown as arrows in Fig. 6a₂ are PPP. Based on AFM imaging, the root-mean-square roughness (RMS) was estimated. The RMS of the untreated film is 5.4 nm . It slightly increases to 5.6 nm after treatment with $1\text{ M H}_2\text{SO}_4$. After the H_2SO_4 treatment, the grains become bigger and elongated and the big PPP grains disappear (see Fig. 6b₁ and b₂). The electrical conductivity of the film has a direct relation to the PEDOT grain size. An increased grain size with decreased grain boundaries leading to few energy barriers will bring about electrical conductivity enhancement [52]. Moreover, charge hopping among the polymer chains is believed to be the dominant conduction mechanism in conducting polymers [53]. Therefore, the H_2SO_4 treated films have more PEDOT-rich areas, and a large portion of the PPP-rich regions was removed, which is in agreement well with the reduction in film thickness. Moreover, the morphology change suggests that the conformation of PEDOT changes from a coiled to a linear/extended-coil structure and reorientation of polymer chains after the H_2SO_4 treatment. The PEDOT-rich chains with a linear structure, larger grain size and lower hopping barriers, can promote charge hopping leading to a higher electrical conductivity.

Compared with the untreated film, the H_2SO_4 treated film with significantly reduced thickness and similar roughness (hence increased surface effect) will increase the phonon scattering, which may be the main reason for the reduced thermal conductivity after treatment.

On the basis of the above results and discussion, the mechanism for the electrical conductivity enhancement of PEDOT-Tos-PPP films after the H_2SO_4 treatment is proposed as follows. First, in a H_2SO_4 aqueous solution at such a high temperature (140°C), the segments of the PPP chains could have rotational and translational motion so that PPP chains moved out from the PEDOT-Tos-PPP film. Second, the partial replacement of the Tos^- ions by SO_4^{2-} ions increases the bipolaron population during an ion exchange process, and, as a consequence, the doping level is increased. In addition, the SO_4^{2-} anions doped in the PEDOT-Tos-PPP films and associated with S^+ of the PEDOT backbone affected the conformation of the polymer chains from a coil structure to a linear or expanded-coil structure (Fig. 7). These changes improve the electrical conductivity dramatically with a concomitant minor reduction of the Seebeck coefficient and a favorite decrease of thermal conductivity. So, an improved ZT value is obtained. Although compared with the PEDOT-Tos films optimized doping in a nitrogen atmosphere reported in Ref. [20], the films

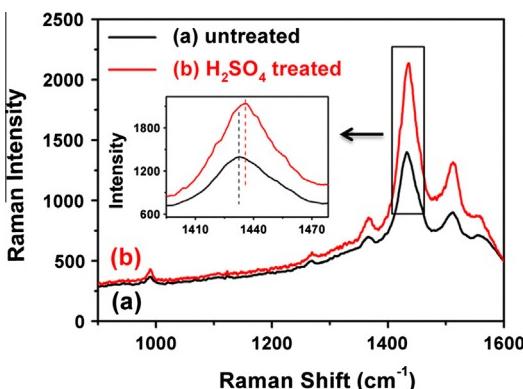


Fig. 5. Raman spectrum of untreated and H_2SO_4 -treated PEDOT-Tos-PPP films.

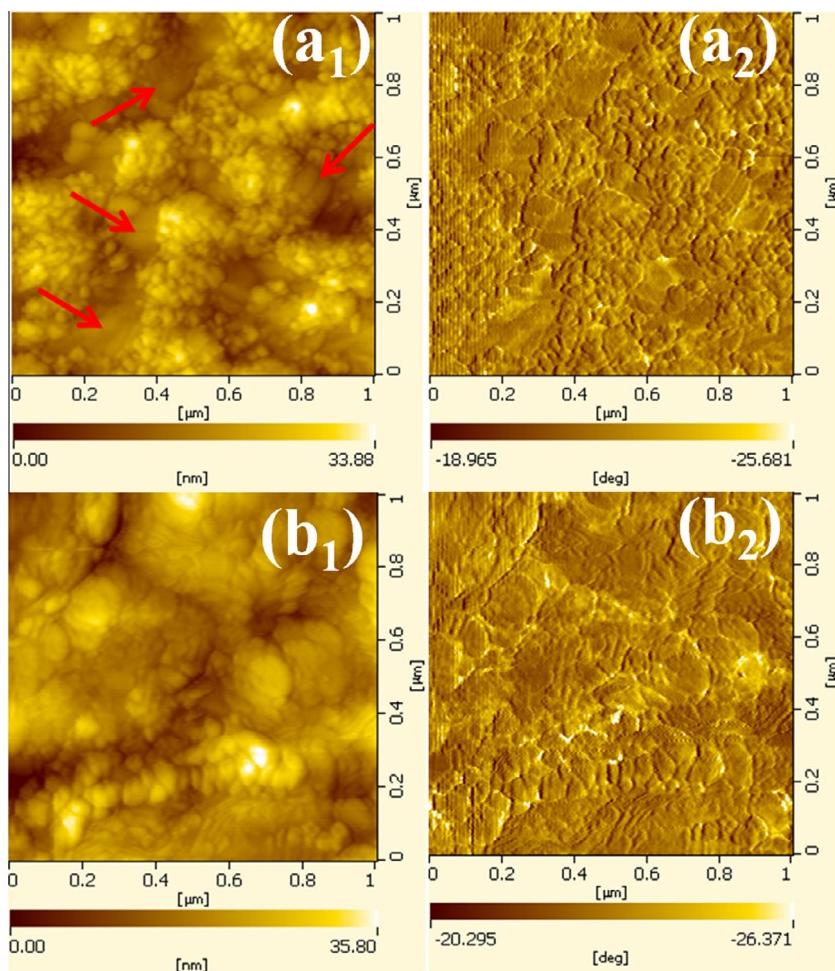


Fig. 6. AFM images of PEDOT-Tos-PPP films before (a₁ and a₂) and after treatment H₂SO₄ (b₁ and b₂), a₁ and b₁ are topographic images; a₂ and b₂ are phase images. All the images are 1 μm \times 1 μm size.

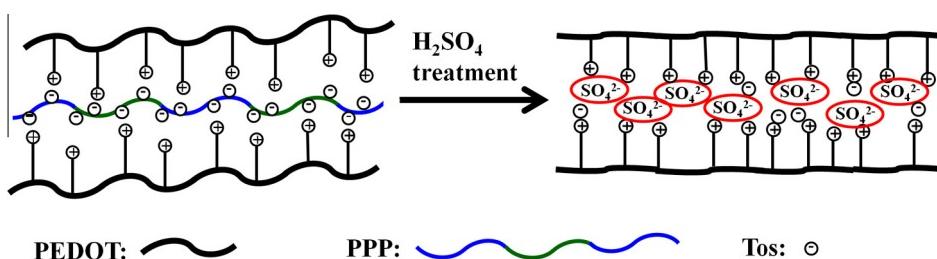


Fig. 7. Schematic structure of PEDOT-Tos-PPP before and after H₂SO₄ treatment.

produced here still show lower ZT values, mainly due to lower Seebeck coefficient, but the method used is simpler and cheaper. A further work, which is under way, is to find out how to increase the Seebeck coefficient without much sacrifice the electrical conductivity of the films.

4. Conclusion

In this paper, a facile VPP method is used to fabricate PEDOT films using tri-block copolymer PPP as a template

to guide self-assembly of PEDOT films. The films are with moderate TE property (power factor $\sim 25.7 \mu\text{W m}^{-1} \text{K}^{-2}$, $ZT \sim 0.016$) for conducting polymers. The electrical conductivity of the films increases dramatically after treated with H₂SO₄, whereas the Seebeck coefficient and thermal conductivity of the films reduce slightly, leading to an enhanced ZT value, 0.024. As the temperature increases from 295 to 375 K, the power factor of the 1 M H₂SO₄ treated film increases from 37.3 to 58 $\mu\text{W m}^{-1} \text{K}^{-2}$. The AFM, XPS, UV-Vis-NIR absorption spectra, and Raman spectra

analyses show that the reasons for the improvement may be the removal of insulating PPP from the PEDOT-Tos-PPP film, increase the doping level and the conformational change of the PEDOT chains after the H_2SO_4 treatment. The combination of the VPP technique and the post treatment is a promising method to fabricate high TE property of polymer films.

Acknowledgements

This work was supported by the National Basic Research Program of China (973 Program) under Grant No. 2013CB632500, National Natural Science Foundation of China (51271133), the Doctoral Program of Higher Education of China (20110072110010), and the foundation of the State Key Lab of Advanced Technology for Material Synthesis and Processing (Wuhan University of Technology).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orgel.2014.09.012>.

References

- [1] B. Poudel, Q. Hao, Y. Ma, Y.C. Lan, A. Minnich, B. Yu, X.A. Yan, D.Z. Wang, A. Muto, D. Vashaee, X.Y. Chen, J.M. Liu, M.S. Dresselhaus, G. Chen, Z.F. Ren, High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys, *Science* 320 (2008) 634–638.
- [2] Y.Z. Pei, X.Y. Shi, A. LaLonde, H. Wang, L.D. Chen, G.J. Snyder, Convergence of electronic bands for high performance bulk thermoelectrics, *Nature* 473 (2011) 66–69.
- [3] K. Biswas, J. He, I.D. Blum, C.-I. Wu, T.P. Hogan, D.N. Seidman, V.P. Dravid, M.G. Kanatzidis, High-performance bulk thermoelectrics with all-scale hierarchical architectures, *Nature* 489 (2012) 414–418.
- [4] I. Levesque, P.O. Bertrand, N. Blouin, M. Leclerc, S. Zecchin, G. Zotti, C.I. Ratcliffe, D.D. Klug, X. Gao, F.M. Gao, J.S. Tse, Synthesis and thermoelectric properties of polycarbazole, polyindolocarbazole, and polydiindolocarbazole derivatives, *Chem. Mater.* 19 (2007) 2128–2138.
- [5] H. Liu, J.Y. Wang, X.B. Hu, R.I. Boughton, S.R. Zhao, Q. Li, M.H. Jiang, Structure and electronic transport properties of polyaniline/NaFeP12 composite, *Chem. Phys. Lett.* 352 (2002) 185–190.
- [6] I. Levesque, X. Gao, D.D. Klug, J.S. Tse, C.I. Ratcliffe, M. Leclerc, Highly soluble poly(2,7-carbazolevinylene) for thermoelectrical applications: from theory to experiment, *React. Funct. Polym.* 65 (2005) 23–36.
- [7] Y. Liao, X.-G. Li, R.B. Kaner, Facile synthesis of water-dispersible conducting polymer nanospheres, *ACS Nano* 4 (2010) 5193–5202.
- [8] Q. Jiang, C. Liu, H. Song, H. Shi, Y. Yao, J. Xu, G. Zhang, B. Lu, Improved thermoelectric performance of PEDOT:PSS films prepared by polar-solvent vapor annealing method, *J. Mater. Sci.: Mater. Electron.* 24 (2013) 4240–4246.
- [9] R. Yue, J. Xu, Poly(3,4-ethylenedioxothiophene) as promising organic thermoelectric materials: a mini-review, *Synth. Met.* 162 (2012) 912–917.
- [10] J. Feng-Xing, X. Jing-Kun, L. Bao-Yang, X. Yu, H. Rong-Jin, L. Lai-Feng, Thermoelectric performance of poly(3,4-ethylenedioxothiophene): poly(styrenesulfonate), *Chin. Phys. Lett.* 25 (2008) 2202–2205.
- [11] Y.Y. Wang, K.F. Cai, X. Yao, One-pot fabrication and enhanced thermoelectric properties of poly(3,4-ethylenedioxothiophene)-Bi2S3 nanocomposites, *J. Nanopart. Res.* 14 (2012) 848.
- [12] Y. Du, K.F. Cai, S. Chen, P. Cizek, T. Lin, Facile preparation and thermoelectric properties of BiTe based alloy nanosheet/PEDOT:PSS composite films, *ACS Appl. Mater. Interfaces* 6 (2014) 5735–5743.
- [13] Y. Du, S.Z. Shen, K.F. Cai, P.S. Casey, Research progress on polymer-inorganic thermoelectric nanocomposite materials, *Prog. Polym. Sci.* 37 (2012) 820–841.
- [14] C.A. Hewitt, A.B. Kaiser, S. Roth, M. Craps, R. Czerw, D.L. Carroll, Multilayered carbon nanotube/polymer composite based thermoelectric fabrics, *Nano Lett.* 12 (2012) 1307–1310.
- [15] Y. Wang, K.F. Cai, X. Yao, Facile fabrication and thermoelectric properties of PbTe-modified poly(3,4-ethylenedioxothiophene) nanotubes, *ACS Appl. Mater. Interfaces* 3 (2011) 1163–1166.
- [16] H. Shi, C. Liu, J. Xu, H. Song, B. Lu, F. Jiang, W. Zhou, G. Zhang, Q. Jiang, Facile fabrication of PEDOT:PSS/polythiophenes bilayered nanofilms on pure organic electrodes and their thermoelectric performance, *ACS Appl. Mater. Interfaces* 5 (2013) 12811–12819.
- [17] Q. Zhang, Y. Sun, W. Xu, D. Zhu, What to expect from conducting polymers on the playground of thermoelectricity: lessons learned from four high-mobility polymeric semiconductors, *Macromolecules* 47 (2014) 609–615.
- [18] M. He, J. Ge, Z. Lin, X. Feng, X. Wang, H. Lu, Y. Yang, F. Qiu, Thermopower enhancement in conducting polymer nanocomposites via carrier energy scattering at the organic–inorganic semiconductor interface, *Energy Environ. Sci.* 5 (2012) 8351–8358.
- [19] O. Bubnova, X. Crispin, Towards polymer-based organic thermoelectric generators, *Energy Environ. Sci.* 5 (2012) 9345–9362.
- [20] Olga Bubnova, Zia Ullah Khan, Abdellah Malti, Slawomir Braun, Mats Fahlman, M. Berggren, X. Crispin, Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxothiophene), *Nat. Mater.* 10 (2011) 429–433.
- [21] G.H. Kim, L. Shao, K. Zhang, K.P. Pipe, Engineered doping of organic semiconductors for enhanced thermoelectric efficiency, *Nat. Mater.* 12 (2013) 719–723.
- [22] O. Bubnova, M. Berggren, X. Crispin, Tuning the thermoelectric properties of conducting polymers in an electrochemical transistor, *J. Am. Chem. Soc.* 134 (2012) 16456–16459.
- [23] N. Massonet, A. Carella, O. Jaudouin, P. Rannou, G. Laval, C. Celle, J.-P. Simonato, Improvement of the Seebeck coefficient of PEDOT:PSS by chemical reduction combined with a novel method to its transfer using free-standing thin films, *J. Mater. Chem. C* 2 (2014) 1278–1283.
- [24] T. Park, C. Park, B. Kim, H. Shin, E. Kim, Flexible PEDOT electrodes with large thermoelectric power factors to generate electricity by the touch of fingertips, *Energy Environ. Sci.* 6 (2013) 788–792.
- [25] J. Luo, D. Billep, T. Waechter, T. Otto, M. Toader, O. Gordan, E. Sheremet, J. Martin, M. Hietschold, D.R.T. Zahn, T. Gessner, Enhancement of the thermoelectric properties of PEDOT:PSS thin films by post-treatment, *J. Mater. Chem. A* 1 (2013) 7576–7583.
- [26] X. Crispin, S. Marciniak, W. Osikowicz, G. Zotti, A.W.D.v.d. Gon, F. Louwet, M. Fahlman, L. Groenendaal, F.D. Schryver, W.R. Salaneck, Conductivity, morphology, interfacial chemistry, and stability of poly(3,4-ethylene dioxythiophene)–poly(styrene sulfonate): a photoelectron spectroscopy study, *J. Polym. Sci. Part B: Polym. Phys.* 41 (2003) 2561–2583.
- [27] J.W. Choi, M.G. Han, S.Y. Kim, S.G. Oh, S.S. Im, Poly(3,4-ethylenedioxothiophene) nanoparticles prepared in aqueous DBSA solutions, *Synth. Met.* 141 (2004) 293–299.
- [28] M. Łapkowski, A. Proń, Electrochemical oxidation of poly(3,4-ethylenedioxothiophene) – “in situ” conductivity and spectroscopic investigations, *Synth. Met.* 110 (2000) 79–83.
- [29] B. Winther-Jensen, D.W. Breiby, K. West, Base inhibited oxidative polymerization of 3,4-ethylenedioxothiophene with iron(III)tosylate, *Synth. Met.* 152 (2005) 1–4.
- [30] M.V. Fabretto, D.R. Evans, M. Mueller, K. Zuber, P. Hojati-Talemi, R.D. Short, G.G. Wallace, P.J. Murphy, Polymeric material with metal-like conductivity for next generation organic electronic devices, *Chem. Mater.* 24 (2012) 3998–4003.
- [31] O. Bubnova, Z.U. Khan, H. Wang, S. Braun, D.R. Evans, M. Fabretto, P. Hojati-Talemi, D. Dagnelund, J.B. Arlin, Y.H. Geerts, S. Desbiez, D.W. Breiby, J.W. Andreassen, R. Lazzaroni, W.M.M. Chen, I. Zozoulenko, M. Fahlman, P.J. Murphy, M. Berggren, X. Crispin, Semi-metallic polymers, *Nat. Mater.* 13 (2014) 190–194.
- [32] Y. Xia, J. Ouyang, Significant conductivity enhancement of conductive poly(3,4-ethylenedioxothiophene): poly(styrenesulfonate) films through a treatment with organic carboxylic acids and inorganic acids, *ACS Appl. Mater. Interfaces* 2 (2010) 474–483.
- [33] D.A. Mengistie, M.A. Ibrahim, P.C. Wang, C.W. Chu, Highly conductive PEDOT:PSS treated with formic acid for ITO-free polymer solar cells, *ACS Appl. Mater. Interfaces* 6 (2014) 2292–2299.
- [34] Y. Xia, J. Ouyang, Highly conductive PEDOT:PSS films prepared through a treatment with geminal diols or amphiphilic fluoro compounds, *Org. Electron.* 13 (2012) 1785–1792.
- [35] J.Y. Kim, J.H. Jung, D.E. Lee, J. Joo, Enhancement of electrical conductivity of poly(3,4-ethylenedioxothiophene)/poly(4-styrenesulfonate) by a change of solvents, *Synth. Met.* 126 (2002) 311–316.

- [36] T.-C. Tsai, H.-C. Chang, C.-H. Chen, W.-T. Whang, Widely variable Seebeck coefficient and enhanced thermoelectric power of PEDOT:PSS films by blending thermal decomposable ammonium formate, *Org. Electron.* 12 (2011) 2159–2164.
- [37] N.F. Mott, E.A. Davis, *Electronic Processes in Non-Crystalline Materials*, Oxford University Press, 1979.
- [38] J.C. Duda, P.E. Hopkins, Y. Shen, M.C. Gupta, Thermal transport in organic semiconducting polymers, *Appl. Phys. Lett.* 102 (2013) 251912–251917.
- [39] D. Alemu, H.-Y. Wei, K.-C. Ho, C.-W. Chu, Highly conductive PEDOT:PSS electrode by simple film treatment with methanol for ITO-free polymer solar cells, *Energy Environ. Sci.* 5 (2012) 9662–9671.
- [40] Y. Xia, K. Sun, J. Ouyang, Solution-processed metallic conducting polymer films as transparent electrode of optoelectronic devices, *Adv. Mater.* 24 (2012) 2436–2440.
- [41] S.G. Im, K.K. Gleason, Systematic control of the electrical conductivity of poly(3,4-ethylenedioxythiophene) via oxidative chemical vapor deposition, *Macromolecules* 40 (2007) 6552–6556.
- [42] S. Garreau, J.L. Duval, G. Louarn, Spectroelectrochemical studies of poly(3,4-ethylenedioxythiophene) in aqueous medium, *Synth. Met.* 125 (2001) 325–329.
- [43] T.C. Chung, J. Kaufman, A. Heeger, F. Wudl, Charge storage in doped poly(thiophene): Optical and electrochemical studies, *Phys. Rev. B* 30 (1984) 702–710.
- [44] M. Fabretto, M. Muller, K. Zuber, P. Murphy, Influence of PEG-ran-PPG surfactant on vapour phase polymerised PEDOT thin films, *Macromol. Rapid Commun.* 30 (2009) 1846–1851.
- [45] M. Fabretto, K. Zuber, C. Hall, P. Murphy, H.J. Griesser, The role of water in the synthesis and performance of vapour phase polymerised PEDOT electrochromic devices, *J. Mater. Chem.* 19 (2009) 7871–7878.
- [46] T.Y. Kim, C.M. Park, J.E. Kim, K.S. Suh, Electronic, chemical and structural change induced by organic solvents in tosylate-doped poly(3,4-ethylenedioxythiophene) (PEDOT-OTs), *Synth. Met.* 149 (2005) 169–174.
- [47] Y. Li, X. Hu, S. Zhou, L. Yang, J. Yan, C. Sun, P. Chen, A facile process to produce highly conductive poly(3,4-ethylenedioxythiophene) films for ITO-free flexible OLED devices, *J. Mater. Chem. C* 2 (2014) 916–924.
- [48] S. Garreau, G. Louarn, J.P. Buisson, G. Froyer, S. Lefrant, In situ spectroelectrochemical Raman studies of poly(3,4-ethylenedioxythiophene) (PEDT), *Macromolecules* 32 (1999) 6807–6812.
- [49] W.W. Chiou, J. Travaš-Šejdić, R.P. Cooney, G.A. Bowmaker, Studies of dopant effects in poly(3,4-ethylenedi-oxythiophene) using Raman spectroscopy, *J. Raman Spectrosc.* 37 (2006) 1354–1361.
- [50] Marisol Reyes-Reyes, Isidro Cruz-Cruz, R.n. López-Sandoval, Enhancement of the electrical conductivity in PEDOT:PSS films by the addition of dimethyl sulfate, *J. Phys. Chem. C* 114 (2010) 20220–20224.
- [51] Y.-K. Han, M.-Y. Chang, W.-Y. Huang, H.-Y. Pan, K.-S. Ho, T.-H. Hsieh, S.-Y. Pan, Improved performance of polymer solar cells featuring one-dimensional PEDOT nanorods in a modified buffer layer, *J. Electrochem. Soc.* 158 (2011) K88–K93.
- [52] Y. Xia, J. Ouyang, PEDOT:PSS films with significantly enhanced conductivities induced by preferential solvation with cosolvents and their application in polymer photovoltaic cells, *J. Mater. Chem.* 21 (2011) 4927–4936.
- [53] A. Aleshin, R. Kiebooms, R. Menon, A.J. Heeger, Electronic transport in doped poly (3,4-ethylenedioxythiophene) near the metal-insulator transition, *Synth. Met.* 90 (1997) 61–68.